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A Sol–Gel Route for the Preparation of Co_3O_4 Catalyst for Oxygen Electrocatalysis in Alkaline Medium

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In order to increase the surface area of oxide electrocatalysts we have studied a new preparation method for Co_3O_4 spinel-type oxides. We have employed a sol–gel route, where the solution of Co(II)-carbonate in propionic acid is heated to form a resinic cobalt propionate. The powder obtained after pouring liquid nitrogen on the gel is immediately thermically treated up to 260°C to obtain the spinel pure phase Co_3O_4, as confirmed by X-ray diffractometry. SEM studies have shown that this precursor phase is near to monodisperse with 2–4 μm particle size. The oxide obtained this way has a BET surface area higher than the oxides prepared by the nitrate decomposition route. However, taking into account the roughness factor, the electrocatalytic activities are similar. © 1994 Academic Press, Inc.

INTRODUCTION

Numerous electrocatalysts have been proposed, among which the cobalt cobaltite, Co_3O_4, of spinel structure, has been intensively studied (1–4). The electrocatalytic properties of oxides can widely vary according to their method of preparation (5). Among the various methods which have been proposed, the thermal decomposition of a solid cobalt salt, principally the nitrate (6), is most frequently used. Other frequently used methods are the ceramic (6) and the chemical spray pyrolysis (7, 8) methods. In contrast, the sol–gel method has been used very little. The sol–gel method involves the transformation of a solution into a gel by ion polymerization, and yields compounds with high surface areas and very narrow particle size distributions (9–12), two properties which are related to the low synthesis temperatures. A sol–gel route is therefore the target of a number of material syntheses. Sol–gel corresponds to potentially interesting technical developments such as dip-coating and spin-coating (13, 14), which could be particularly useful for electrode preparation in electrochemistry. Thus, the preparation of oxide electrocatalysts by sol–gel seems very promising. We present here preliminary results related to Co_3O_4: a description of the method, characterization of the product, and comparison with the compounds which are obtained by solid state nitrate decomposition and spray pyrolysis of nitrate aqueous solutions.

METHODS OF PREPARATION OF Co_3O_4

Sol–Gel

We first prepared pure anhydrous cobalt carbonate, $CoCO_3$, by addition of sodium carbonate, Na_2CO_3 (Alfa, Ref. 307528), to a concentrated aqueous solution of cobalt nitrate, $Co(NO_3)_2\,6\,H_2O$ (Merck, Ref. 2536). After precipitation, filtration, and washing, the $CoCO_3$ powder was dissolved in liquid propionic acid, CH_3CH_2COOH (Janssen, Ref. 149 089). The solution was heated at 140°C so that most of the excess of propionic acid was evaporated until a gel was formed. Liquid nitrogen was then added rapidly, thus powdering the gel into solid state cobalt propionate $(CH_3CH_2CO_2)_2Co$. The cobalt propionate powder was then again heated at 180°C for 1 hr for more complete removal of the propionic acid. The powder of $(CH_3CH_2CO_2)_2Co$ was finally treated, in air, at different temperatures in the range 250–450°C, yielding cobalt oxide phases. The temperature of 260°C was found to be a threshold to obtain the pure spinel phase Co_3O_4, as the oxide of cobalt CoO was the only product below 260°C (see below).

Thermal Decomposition of Solid Nitrate

$Co(NO_3)_2\,6\,H_2O$ (Merck, ref. 2536) was allowed to dissolve in its crystallization water by gradually heating it up to 100°C. The solution was then evaporated and the residual solid nitrate was further decomposed in air at 380°C for 4 hr (15).

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TABLE 1

Miller Indexes (*hkl*), Interplanar Spacings, *d* (Å), and Relative Intensities I/I_{max}, of Diffracted X-Rays Beams of the Oxides Issued of the Calcination of the Sol–Gel Cobalt Propionate $(CH_3CH_2CO_2)_2Co$ (Sol–Gel), the Thermal Decomposition of $(NO_3)_2Co$, 6 H_2O (Nitrate Decomp.), and Chemical Spray Pyrolysis of an Aqueous Solution of $(NO_3)_2Co$, 6 H_2O (Chem. Spray Pyrol.), at Various Temperatures

Sample	Temp. (°C)	Annealing time, (hr)	111		200		220		311	
			d	I/I_{max}	*d*	I/I_{max}	*d*	I/I_{max}	*d*	I/I_{max}
Sol–gel	250	1	2.459	64	2.130	100	1.505	52	1.285	19
ASTM (9-402)			2.460	75	2.130	100	1.506	50	1.285	20
			111		220		311		222	
			d	I/I_{max}	*d*	I/I_{max}	*d*	I/I_{max}	*d*	I/I_{max}
Sol–gel	280	1	4.671	32	2.859	45	2.444	100		
	300	1	4.678	38	2.859	54	2.44	100	2.340	24
	350	1	4.670	32	2.860	45	2.438	100	2.332	28
	380	2	4.663	29	2.859	43	2.439	100	2.339	26
Nitrate decomp.	380	4	4.665	16	2.853	34	2.433	100	2.332	8
Chem. Spray Pyrol.	350–400	Without object	4.684	34	2.860	45	2.439	100	2.338	23
ASTM (9-418)			4.669	20	2.860	40	2.438	100	2.333	12

Note: ASTM files are given for the sake of comparison: ASTM (9-402): CoO, ASTM (9-418): Co_3O_4.

Chemical Spray Pyrolysis of Nitrate Solutions

In this method, the decomposition of the nitrate was conducted by spraying an aqueous solution of $Co(NO_3)_2$, $6H_2O$ (Merck, Ref. 2536) on a substrate heated at 350–400°C, and placed on a heating plate. Details have been given previously (7). When the substrate is an electrical conductor, a thin oxide film electrode is directly obtained with this method.

CHARACTERIZATION OF THE COMPOUNDS

X-Ray Diffraction

Diffractograms were obtained with a Guinier–Wolf chamber using the Co$K\alpha$ radiation. Table 1 shows that when the cobalt propionate sol–gel powder was directly heated at constant temperature in an oven, the CoO was the only phase at 250°C; the pure Co_3O_4 phase appeared

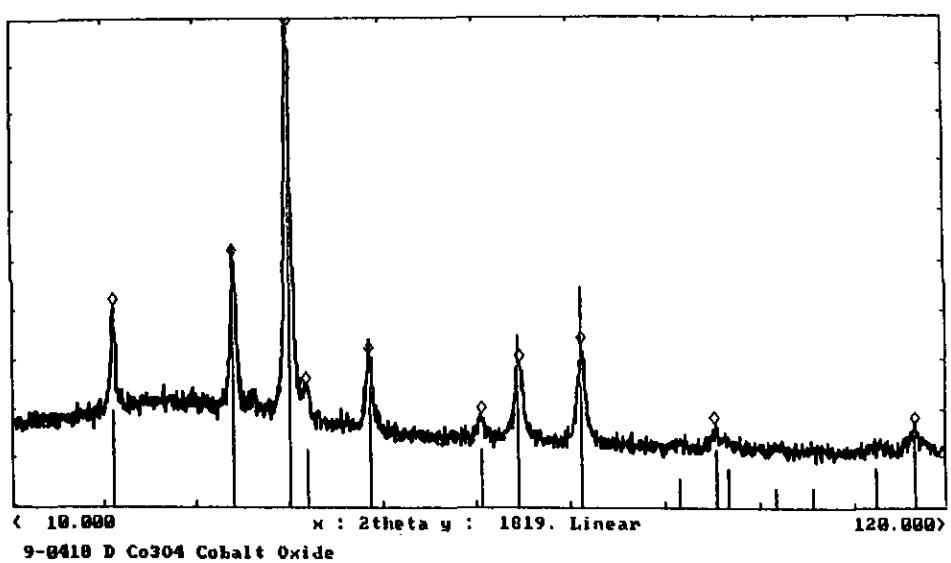

FIG. 1. Diffractogram of the product obtained after calcination in air of the sol–gel cobalt propionate $(CH_3CH_2CO_2)_2Co$ at 300°C: Co_3O_4.

TABLE 1—*Continued*

222		400	
d	I/I_{max}	d	I/I_{max}
1.231	18	1.065	9
1.230	16	1.065	10

400		422		511		440		533		731	
d	I/I_{max}	d	I/I_{max}	d	I/I_{max}	d	I/I_{max}	d	I/I_{max}	d	I/I_{max}
2.030	39	1.651	20	1.557	42	1.430	46	1.227	36	1.053	38
2.022	32	1.650	19	1.556	31	1.431	33	1.232	17	1.052	17
2.020	38	1.646	23	1.557	38	1.429	41	1.232	22	1.053	22
2.021	32	1.651	23	1.556	33	1.428	38	1.232	24	1.053	31
2.018	23	1.649	12	1.555	34	1.428	44	1.232	10	1.052	14
2.022	26	1.652	16	1.556	23	1.429	28	1.231	14	1.051	12
2.021	25	1.650	12	1.556	35	1.429	45	1.233	12	1.052	16

only at 280°C and above. The degree of crystallinity increases with the temperature. Figure 1 shows the diffractogram of Co_3O_4 sol–gel obtained at 300°C. The product is well crystallized and no diffraction peaks other than those of Co_3O_4 were present. Figure 2 shows that the parameter a of the cubic cell of Co_3O_4 sol–gel decreases less with increasing temperatures of calcination than it does with the nitrate decomposition product. This is to be related with the TG results (see below).

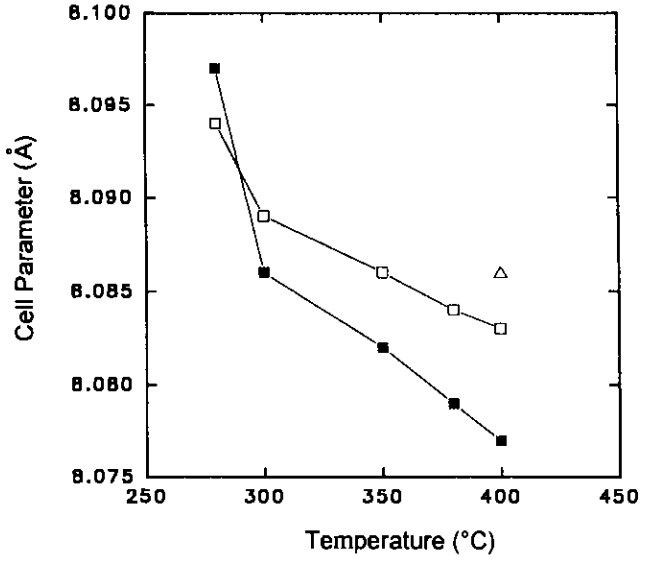

FIG. 2. Variation of the Co_3O_4 cubic cell parameter a, in Å, with temperature for three methods of preparation: (□) sol–gel (■) decomposition of solid state nitrate (△) chemical spray pyrolysis on Ti.

Scanning Electron Microscopy

Figures 3a–3d show microphotographs corresponding to sol–gel, solid state nitrate decomposition and chemical spray compounds, obtained with a Jeol scanning electron microscope. The sol–gel compound shows a very narrow particle size distribution around 2–4 μm (Fig. 3d), in contrast with the chemical spray compound, which is rather compact. To obtain these pictures, the sol–gel powder had been spread onto a conductive substrate from its suspension in isopropylic alcohol. Electrodes of this type, made of the sol–gel compounds, have a higher porosity and a higher surface area than those made of powders obtained by the ceramic or solid state nitrate decomposition method, Fig. 3b, or directly obtained by chemical spraying, Fig. 3c.

Thermogravimetric, Differential Thermal, and Mass Spectroscopic Analyses

The loss of weight during the combustion of the cobalt propionate $(CH_3CH_2CO_2)_2Co$ sol–gel powder in air, at constant pressure and different temperature rates, was measured using a TG–DTA Setaram 92 thermogravimetric + differential thermal analysis apparatus. The gaseous by-products were analyzed simultaneously by mass spectroscopy, the apparatus being coupled with a multichannel mass spectroscopy analyzer.

We observed that the rise in temperature had to be kept below 0.1°C mn^{-1} in order to avoid excessive heat flow, and even explosive reactions around 220–260°C. Figure 4 shows the shape of the thermograms, together with a

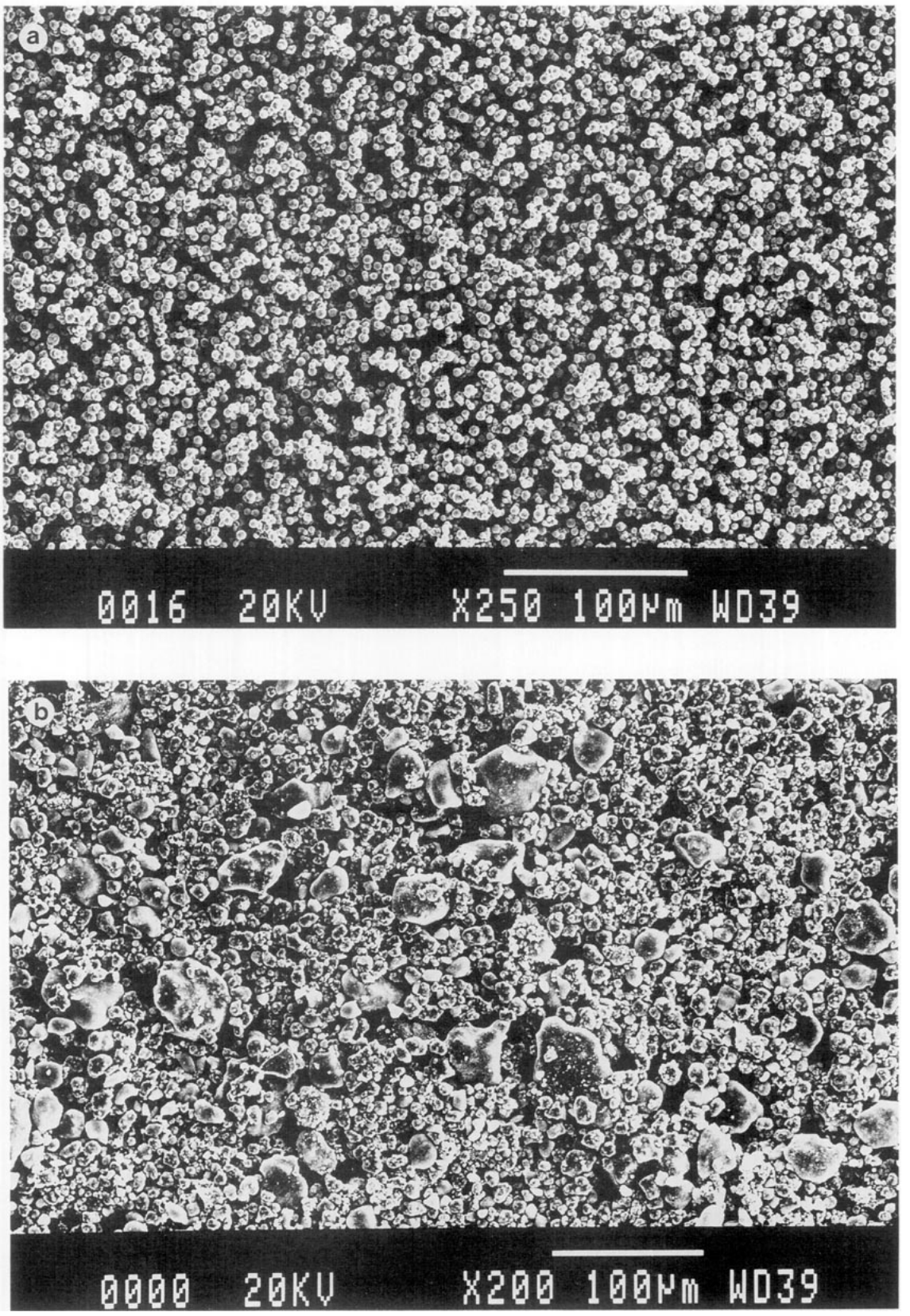

FIG. 3. Scanning electron microscopy microphotographs of Co_3O_4 powders prepared by (a) sol–gel (b) nitrate decomposition (c) chemical spray pyrolysis (d) sol–gel at a higher magnification.

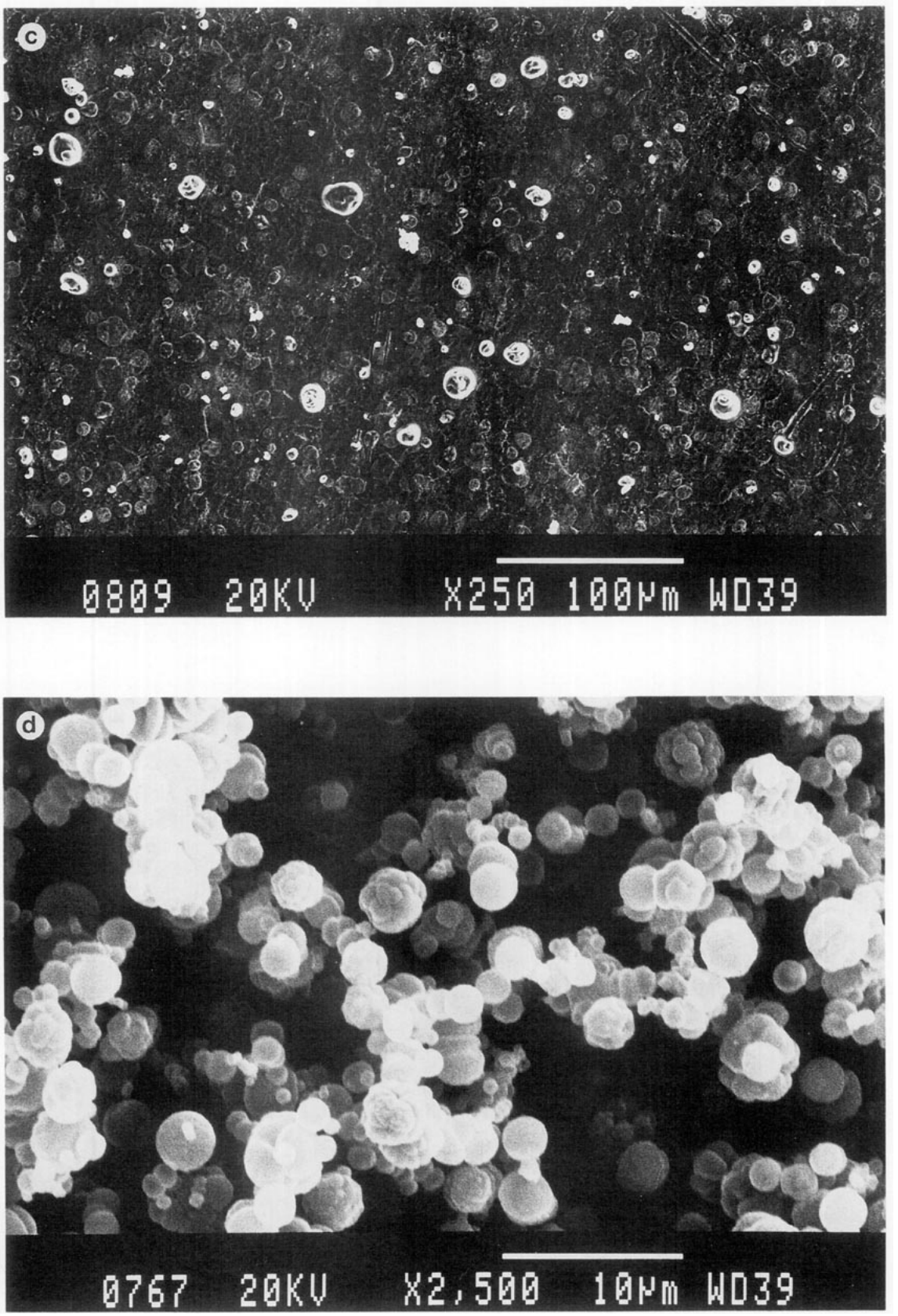

FIG. 3—*Continued*

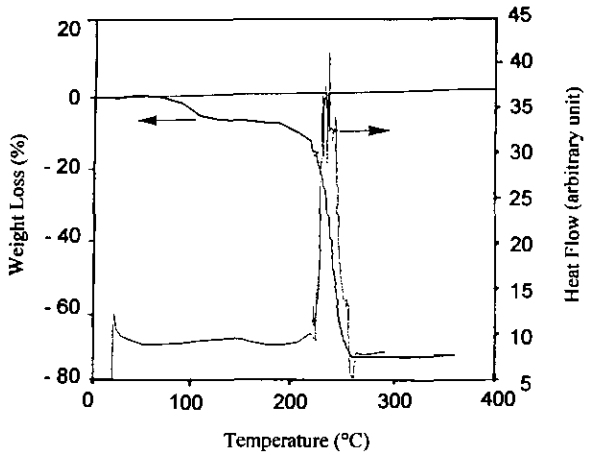

FIG. 4. Loss of weight and heat flow with temperature during the calcination in air of the sol-gel cobalt propionate $(CH_3CH_2CO_2)_2Co$; atmospheric pressure; heating rate: 6°C hr^{-1}.

heat flow peak. The percentage of the loss of weight between 150 and 350°C was 64%, compared with 61% for the global reactions:

$$7O_2 + (CH_3CH_2CO_2)_2Co \rightarrow 6CO_2\nearrow + 5H_2O\nearrow + CoO$$

coupled with

$$O_2 + 6CoO \rightarrow 2Co_3O_4.$$

When the cobalt propionate powder was directly heated at constant temperature in an oven, X-ray analysis had shown (see above) that CoO was the only product below 250–280°C. Therefore, the oxide of cobalt CoO is likely to be an intermediate in the synthesis of Co_3O_4. An additional proof is given by mass spectroscopy analysis of the gaseous products during calcination, which shows, together with CO_2 and H_2O gases, the occurrence around 230°C of the radical CH_3CH_2CO, of mass 57 (beside traces of $M = 73$ $(CH_3CH_2CO_2)$ and $M = 74$ (CH_3CH_2COOH)).

The thermal decomposition of solid state $(NO_3)_2Co, 6H_2O$ was compared to the thermal decomposition of $(CH_3CH_2CO_2)_2$ Co using the same apparatus. The decomposition occurs via the global reaction:

$$3(NO_3)_2\,Co, 6\,H_2O \rightarrow 6\,H_2O\nearrow + 2\,NO_2\nearrow + 2\,N_2O_5\nearrow + Co_3O_4.$$

The decomposition is more complex. Co_3O_4 was obtained at 260°C, but kept losing weight when continuously heated above 260°C; this process continued even during the cooling back stage, after having reached 500°C. This behavior has been previously noted (16, 17) and describes the varying stoichiometry in oxygen with temperature of cobaltites whose formula is $Co_3O_{4+\delta}$. It is noteworthy that with the sol–gel compound, this does not occur, the reverse curve lying on top of the forward one. This shows that the sol–gel phase has an invariant excess oxygen, δ, with temperature, in contrast with the phase obtained by solid state nitrate decomposition.

TABLE 2
Surface Areas of the Co_3O_4 Powders from BET Measurements

Annealing temperature (°C)	Sol–gel ($m^2 \cdot g^{-1}$)	Nitrate decomposition ($m^2 \cdot g^{-1}$)	Ref. (15) ($m^2 \cdot g^{-1}$)
300	28	20	23
350	19	16	14, 5
400	14	10	10
450	8	5	5, 8

Surface Area

The surface area of the Co_3O_4 powders was measured with a Sorpty 1750 Carlo Erba instrument by the BET method, using nitrogen gas absorption at liquid nitrogen temperature. Table 2 presents the surface areas of the Co_3O_4 powders prepared by sol–gel and solid state nitrate decomposition. For the sake of comparison, data from the literature are also provided (15). At all annealing temperatures the sol–gel compound presents a higher surface area than the compounds which are prepared by the other methods.

Electrical Conductivity

The electrical conductivity of Co_3O_4 prepared by sol–gel and solid state nitrate decomposition was directly measured with a Keithley 227 ohmmeter on pellets of the powders and on the two faces of which ohmic contacts were made to Cu wires, using silver paste. For the films of Co_3O_4 deposited by spray pyrolysis on Pyrex glass, the four point probe method was used. Results are shown in Tables 3 and 4: spray pyrolysis films have higher conductivities, varying with thickness, but the sol–gel compound has a higher conductivity than the compound obtained

TABLE 3
Electrical Conductivities, σ, in Ω^{-1} cm^{-1}, as a Function of Temperature of Co_3O_4 Sol–Gel and Co_3O_4 from the Decomposition of the Cobalt Nitrate

	Temperature			
	280°C	300°C	350°C	400°C
Co_3O_4 Sol–gel	3×10^{-4}	15×10^{-4}	65×10^{-4}	180×10^{-4}
Co_3O_4 Nitrate decompos.	1×10^{-4}	4×10^{-4}	9×10^{-4}	21×10^{-4}

TABLE 4

Electrical Conductivities of Films of Co_3O_4 on Pyrex Glass Prepared by Chemical Spray Pyrolysis at 350–400°C as a Function of Thickness

Thickness (μm)	3.4	3.1	1.7
σ (Ω^{-1} cm^{-1})	120×10^{-4}	300×10^{-4}	800×10^{-4}

from the thermal decomposition of solid state nitrate. The ratio of the conductivities increases from 3 to 9 from 280 to 400°C, giving to the sol–gel compound a conductivity which is comparable to the conductivity of thick sprayed films prepared at 350–400°C. This might be due to the particular morphology of the sol–gel product, which is made of nearly monodisperse particles, thus favoring good contacts between grains. The values compare quite well with literature (6, 18–19).

ELECTROCHEMICAL PROPERTIES

The Co_3O_4 powders prepared by either the sol–gel method and the solid state nitrate decomposition have conductivities and mechanical properties which lend themselves to forming electrodes simply by pelletizing the pure phase. The resistance of the electrode is too high and the pellets decompose in solution. Mixing with graphite powder makes it possible to obtain pellets which work as electrodes for practical use, but it becomes difficult to determine what part of the electrochemical response is due to the oxide and what part is due to the graphite. According to some authors, graphite is activated by the oxide in such intimate mixtures (2, 20, 21). Attempts to form electrodes by dip-coating of the gel onto conductive substrates have been unsuccessful. To overcome these difficulties, electrodes were obtained by painting the oxide suspension in isopropanol on an polyisobutylene foil (Nikolaus Branz, Berlin) charged with graphite of the type used by the battery industry. No pressure was applied. In that case, the carbon material acts only like a substrate. After annealing at 200°C a good adherence was obtained.

A cyclic voltammogram was observed with the classical shape, showing the usual redox peaks of the Co^{IV}/Co^{III} surface redox couple just prior to oxygen evolution, as repeatedly shown in the literature (8, 22, 23). Figure 5 shows the cyclic voltammogram of the Co_3O_4 sol–gel electrode. Their roughness factor (i.e., the ratio between the real surface area and that corresponding to an ideally flat surface) was determined by cyclic voltammetry between 0 and 80 mV vs HgO/Hg/1 *M* KOH, i.e., in the double-layer region, yielding clear capacitive currents (24). In our view, the criticisms which were occasionally expressed

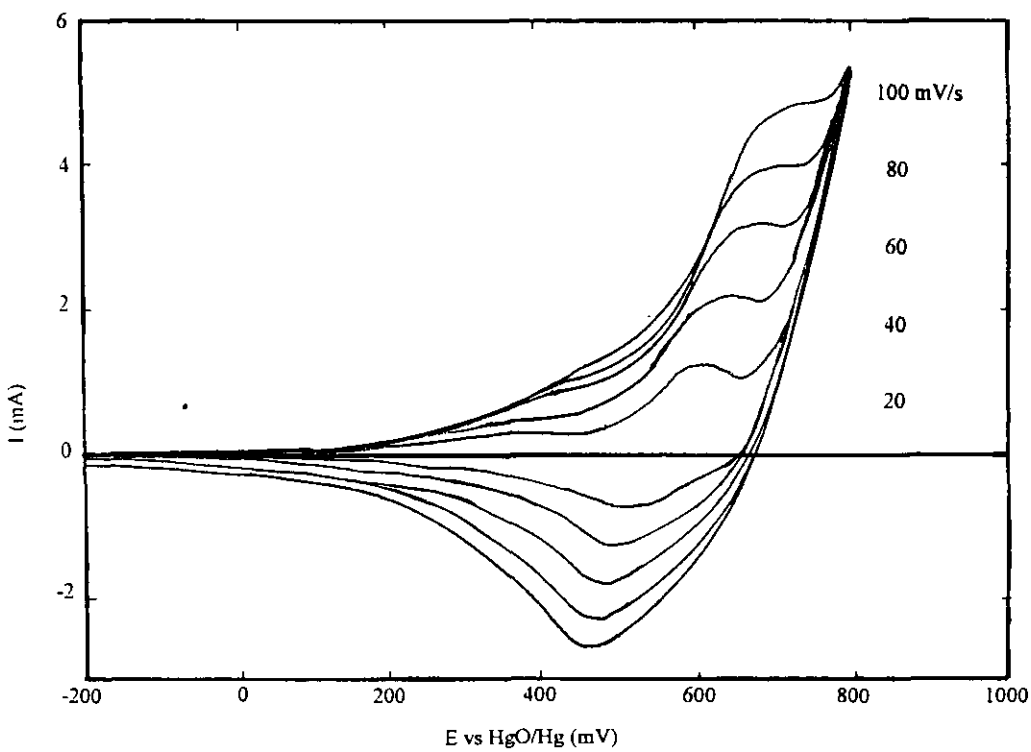

FIG. 5. Cyclic voltammogram of Co_3O_4 sol–gel in 1 *M* KOH at different scanning rates, in mV sec^{-1}.

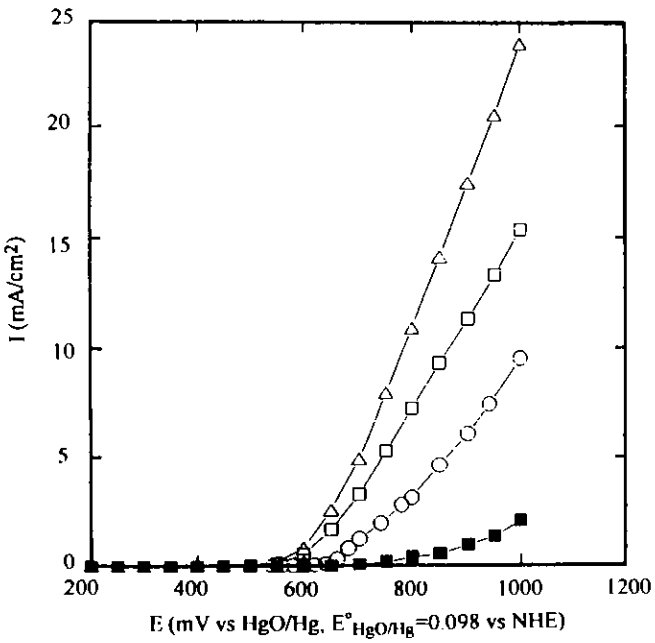

FIG. 6. Kinetics of the evolution of oxygen on Co_3O_4 electrodes in 1 *M* KOH (△): sol–gel, (□): decomposition of solid state nitrate, (○): chemical spray pyrolysis on Ti, (■): bare substrate (graphitized polyisobutylene).

against the method, which requires the knowledge of the differential capacity of the interface oxide aqueous electrolyte, and taken as 60 μF cm^{-2}, do not apply here, as we are comparing the same oxide phases synthesized by different methods.

With Co_3O_4 obtained by spray pyrolysis on titanum the roughness factor is only 5, whereas with Co_3O_4 from solid state nitrate decomposition on polyisobutylene it is approximatively 18; with Co_3O_4 sol–gel on graphite polyisobutylene, it is 33, i.e., seven times higher. Comparing to the data in Table II, one sees that the ratios were, respectively, 1.8 and 1.4 between the BET surface areas and the roughness factors of the sol–gel and nitrate decomposition products. One has to expect that the powder with a higher BET surface leads to a coating with a higher roughness factor, which is indeed the case here, the ratios being only approximatively of the same order of magnitude.

Figure 6 shows that higher currents per geometric unit area for the evolution of oxygen are obtained with electrodes made of the sol–gel Co_3O_4 phase than with electrodes made of the Co_3O_4 phase obtained from the decomposition of the solid state cobalt nitrate or chemical spray pyrolysis. This is undoubtedly due to higher roughness of the sol–gel Co_3O_4. However, if the roughness factor is taken into account, one sees that the true electrocatalytical activities of the Co_3O_4 sol–gel and of the nitrate decomposition Co_3O_4 are similar, the true electrocatalytical activity of the sprayed Co_3O_4 being higher. Dividing the current densities at 1 V vs Hg/HgO/1 *M* KOH (Fig. 6) by the roughness factor yields the current densities per real surface unit area, in mA cm^{-2} (real): 0.7 (sol–gel) ≈ 0.7 (nitrate decomposition) < 1.4 (spray).

CONCLUSION

In this work we have shown that a sol–gel route is available for the preparation of Co_3O_4. This new method is a simple one which allows the preparation of a stable pure phase at relatively low temperature (280°C). The Co_3O_4 powder has a narrow particle size distribution. Its real surface area is higher than that obtained by other methods, such as solid state nitrate decomposition and spray pyrolysis of aqueous nitrate solution. The electrical conductivity was found to lie between that of the compounds obtained by decomposition of nitrate and spray pyrolysis.

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